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A Study of the Ignition Kinetics of XM46

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Raymond Von Wahlde, and Joyce E. Newberry

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Abstract

Preliminary results in an attempt to define the ignition kinetics of the liquid propellant XM46 under high-heating rates are reported. Three methods of approach have been applied: (1) conventional differential scanning calorimetry (DSC), (2) a drop of the liquid floating in an inert, heated liquid, and (3) CO₂ laser heating. In the latter case, the delay to pressure release has been studied as a function of prepressurization over the range from 3 to 14 Mpa (500 to 2,000 psi). Expressed as delay (ms) = $C \exp(E_a/RT)$, values measured are $C = 2.48$ and 2.45 and $E_a = 7.7 (\pm 4.9)$ and $1.9 (\pm 1.2)$ kcal/mol at pressures of 6.9 Mpa (1,000 psi) and 9.7 Mpa (1,400 psi), respectively. The temperature of the liquid used for analysis of the laser heating experiments is calculated. The ignition (reaction) delays show a strong temperature and pressure dependence. High-speed photography shows that the pressure rise is not from ignition of the small volume where the energy is absorbed, but is rather from a partial reaction involving most of the liquid in the vessel.

Acknowledgments

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1. Introduction

In the efforts to understand and control the ignition process of the regenerative liquid propellant gun (RLPG), a key missing parameter is the time to ignition and full heat release of the propellant XM46. That is, while much progress has been made in detailing the pathways to reaction, interior ballistic models require a parametric dependence of propellant energy release as a function of time and temperature.

XM46 is a stoichiometric homogeneous combination of hydroxylammonium nitrate (HAN) (63.2%), triethanol ammonium nitrate (TEAN) (20.0%), and water (16.8% by weight). It can be described as either an ionic aqueous solution or as a molten salt.

In order to study ignition, a working definition of ignition is required. Since this propellant does not burn with substantial energy release below pressures of 10 to 15 MPa, ignition (meaning the process that leads directly to major energy release) beginning at atmospheric pressure will tend to be strongly dependent on the geometry of the test device. This effect arises because of the self-pressurization following gas release, which will strongly affect the observed rates and processes. In many studies of the ignition of energetic materials, ignition has been assumed to begin with the first major exotherm. For XM46, this exotherm has been observed to occur near 120 °C; this reaction has been attributed to the decomposition of HAN [1]. This temperature is sometimes referred to as the "ignition temperature" of the propellant. The "accepted" value for ignition thus defined has typically been 120 °C to 140 °C. This approach of assigning the first indication of exothermic reaction as "ignition" is followed in the present study.

It was originally a goal to delineate the pathways and specific rates of the various steps that together make up the ignition of the propellant XM46. However, due to the immediate needs of modelers and others in the gun development program, the modest goal here has been to measure the time to heat release as a function of pressure and temperature. As with many studies before,

it was assumed at the outset that the initial reaction controls the combustion mechanism and that any subsequent reactions will be relatively fast.

2. Background and Approach

The backbone of kinetics studies with solid gun propellants has been the standard analytical chemistry technique known as differential scanning calorimetry (DSC). By a straightforward heating of the material under well-controlled conditions and recording endothermic and exothermic events, ignition temperatures and kinetics can be developed. The difficulty of using this same approach with XM46 has been noted. However, Fifer et al. [2] demonstrated that they may have been close to achieving at least reproducibility. Other more recent communications [3] have also verified that this may be possible with the use of special materials such as well-aged aluminum or gold-plated DSC pans. Therefore, this method was chosen as a possible baseline for studies, in spite of the limitation of the relatively slow rates at which the material can be heated and possible catalytic effects due to contact with the sample pans.

The second method that was adopted for application in the present work is the floating of a drop of the propellant in an inert liquid that is sufficiently heated to cause reaction. This technique was used earlier by Law [4] to study the closely related propellant LP1845. A most interesting observation of that study was that the "explosion" (i.e., fast reaction) temperature of this liquid propellant (LP) was found to be about 230 °C. This much higher number than the 140° C that has been "accepted" from early DSC measurements then leads to speculation on the possible role of surface-enhanced reactions in any other reaction study. That is, the floating-drop technique is expected to be immune to surface effects that might lower the temperature of reaction onset. It was hoped at the outset to use this technique to study the effect of pressure.

The third approach used is the heating of the propellant with a carbon dioxide (CO₂) laser. The basis of this method is the extensive work [5] on laser ignition of this same propellant, but with the change in laser to make the interaction dominated by thermal effects. The primary

limitation here is the lack of a measurable temperature in the liquid. The temperature is calculated from the measured optical absorption of the liquid and the laser beam parameters.

3. Observations

3.1 DSC. DSC is a well-established technique for determining the chemical kinetics of energetic materials. Almost equally well established is the difficulty of using it to learn about XM46 kinetics (for example, see Fifer et al. [2]). Much of the difficulty takes the form of inconsistent and nonreproducible results. The source of such problems is probably the chemical interaction of the liquid with the sample holder. Other possible causes include the relatively large surface-to-volume ratio of the small sample sizes that are required for this technique. High surface ratios can allow changes in the percent of water in the composition by absorption to or loss from the sample to the laboratory air [6]. The DSC studies of Fifer et al. [2] showed that consistent, reproducible results might well be obtainable with proper materials. This conclusion is supported by the consistent ignition temperatures that have been obtained when tantalum vessels are used. This consistency could be interpreted as a apparent lack of reaction between the XM46 and tantalum.

The present studies started with the capability to prepressurize the DSC to pressures up to 7 MPa (1,000 psi) and with several materials possible for the sample pans. However, these efforts have not yielded results of substance. Some trends have been observed, and they are reported briefly. A standard method of obtaining reproducible results with energetic materials is to use a closed pan with a tightly crimped cover. A small pin-sized hole in the cover avoids pressurization from slow gas evolution, and an argon purge of the sample area is used to remove gas-phase reaction products. Figure 1 shows the results of such a test using an aged aluminum pan at a heating rate of 2 °C/min. As can be seen in the figure, there is little activity before the major exotherm near 180 °C. A series of well-behaved records like this one, if consistently reproducible, would present the researcher with a good start toward understanding the kinetics of this first major exotherm. Such was not to be the case, as the data scattered at random.

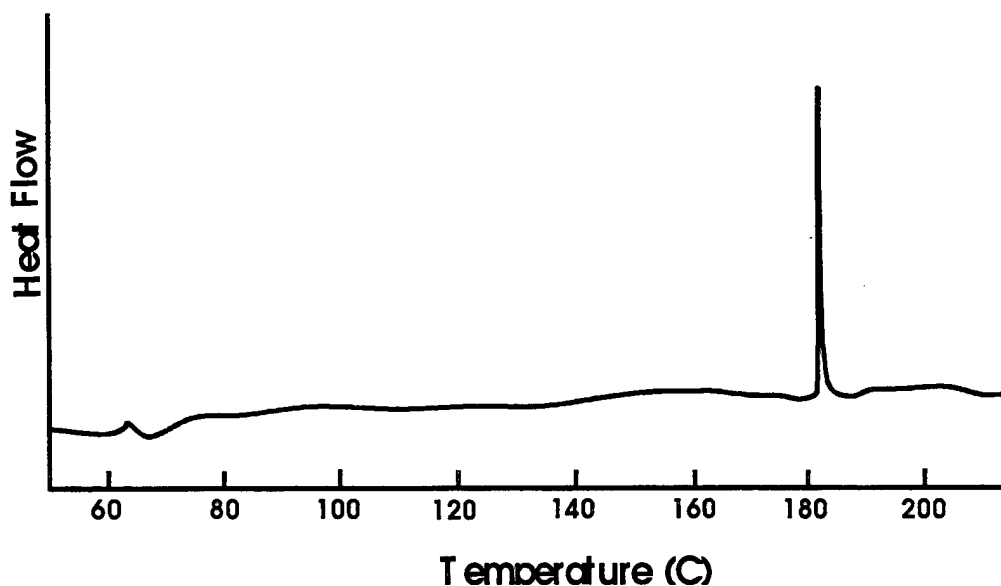


Figure 1. Typical DSC Record Done in Pierced, Crimped Aluminum Pan.

Since the problem with “fresh” aluminum pans has been postulated to be due to a chemical reaction of the propellant with the aluminum [3], a series of observations was made using the “nonreactive” (or at least consistent) tantalum. The first test with an in-house-made tantalum pan, crimped in somewhat the same manner as the standard aluminum pans, yielded an exotherm near 90 °C (rate 5 °C/min), which consumed the liquid and left only a small amount of solid residue. A series of tests was then made to compare the tantalum with the least-reactive material readily available, glass. Because the glass was used in an flat, open-pan configuration, the metal was also used this way. The tantalum exotherms were reproducible and consistently at lower temperatures than those with glass. In addition, the tantalum almost always showed a “sputtering” prior to the exotherm. An example heated at 5 °C/min is shown in Figure 2. The broad endotherm near 80 °C has been attributed to the loss of water [3]; this conclusion was neither verified nor disproved. A sample heated on glass under as nearly the same conditions as possible is shown in Figure 3. As can be seen, the early endotherm is similar, but the exotherm is clean and occurs at a significantly higher temperature. A series of runs on glass to determine if reproducibility adequate for quantification of the kinetics could be achieved yielded scattered, inconsistent results.

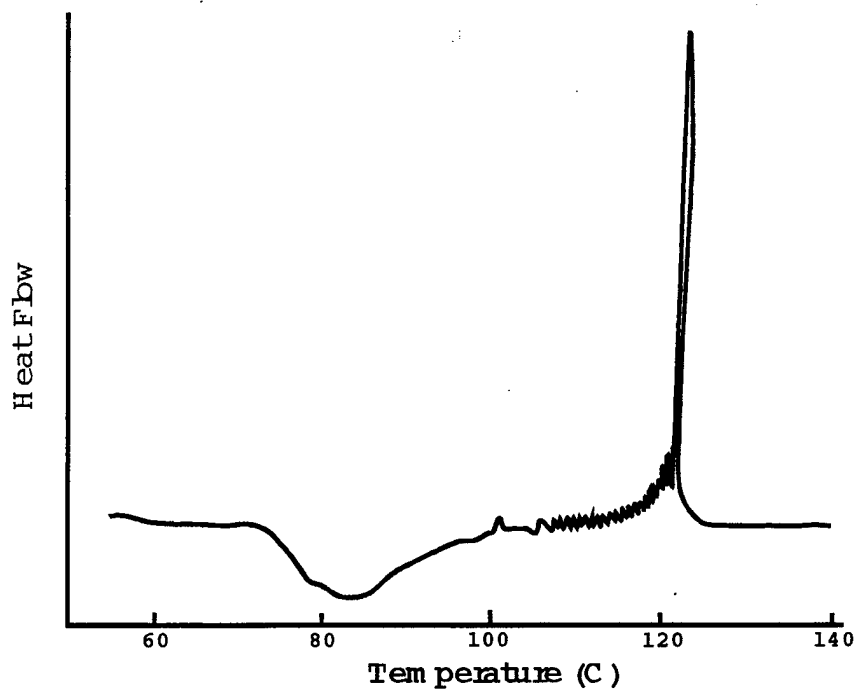


Figure 2. Record From DSC Test of XM46 on Tantalum Plate.

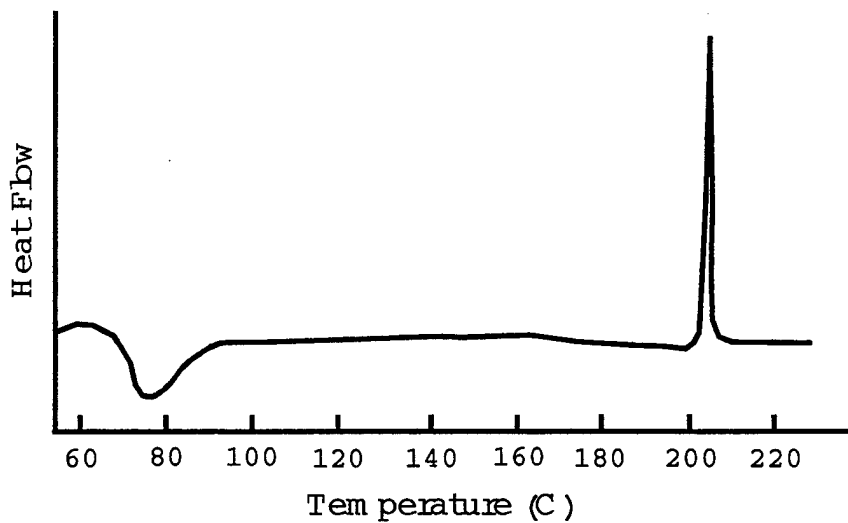


Figure 3. DSC Record for XM46 Done on Glass Plate.

3.2 Floating-Drop Experiments. The liquid used in these observations was perfluoroalkylether (Dupont "Krytox 143AD"). It has a density of 1.90 g/cm^3 at 25°C and 1.60 g/cm^3 at 200°C , which provides a sufficient buoyancy for the XM46 with a density of

1.43 g/cm³ at ambient. A simple apparatus (shown schematically in Figure 4) was constructed to study the behavior at atmospheric pressure; in particular, a verification of the 230 °C explosion temperature observed by Law [4] was desired. Several observations were made with both the propellant and water, which confirmed the reported value. The next step would have been to build an apparatus that could function under pressure, in order to study the explosion temperature as a function of that parameter. However, with the limited buoyancy, there was some difficulty in separating the LP drops from the syringe. It is not desirable to use any electric current or strong electric fields to facilitate the separation. Because of this, the design of the apparatus became more complicated than the end results justified, and it was suspended. As they are not widely available, Law's results of LP 1845 (with added water) vs. water concentration are reproduced in Figure 5. Because the values of explosion temperature are not much different from that of pure water, the question remains as to whether this observation is dominated by water vaporization, with the possibility that chemical reaction is initiated at even higher temperatures unless a solid surface is present.

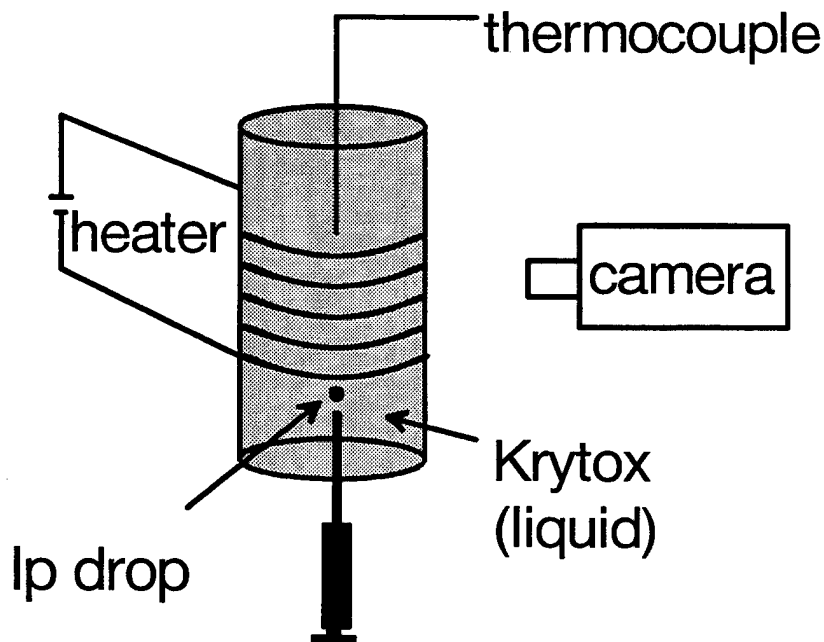


Figure 4. Schematic of Apparatus for Heating Drop in Inert Liquid.

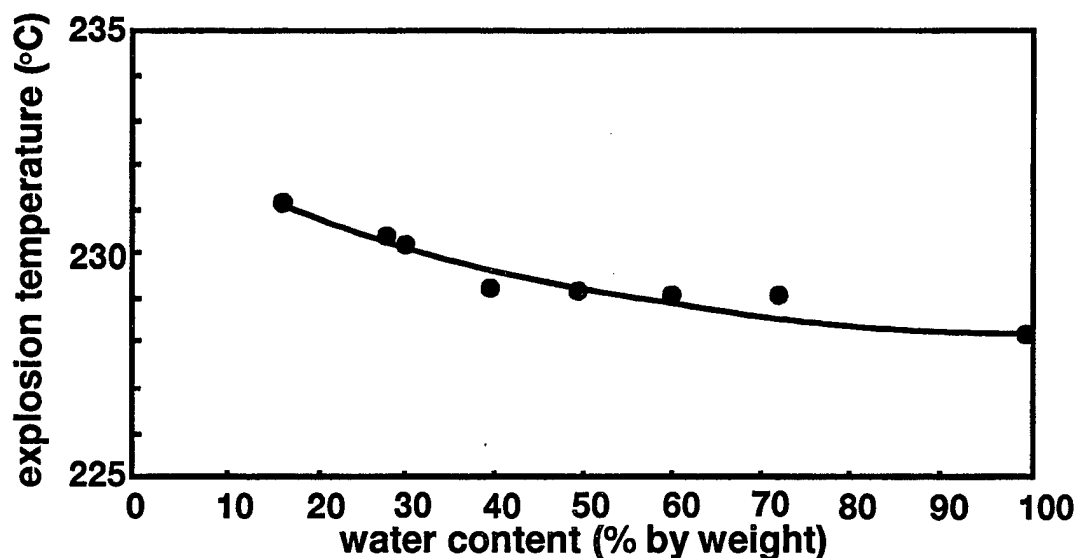


Figure 5. Explosion Temperature of LP 1845 With Added Water as a Function of Total Water Content [4].

3.3 Laser-Heated Experiments.

3.3.1 Reaction Delay Time. The goal of this series of observations was to provide a technique that could provide rapid heating of the propellant (at rates comparable to those in the gun), at a range of well-controlled pressures, but with the propellant not in contact with a solid surface at the heating point. A schematic diagram of the apparatus is shown in Figure 6. The prepressurization is provided by argon gas. The gas-phase gap between the upper (heated) surface of the liquid and the ZnSe window avoids the possibility of solid-surface influence on the ignition process, as well as protecting the window from reaction at its surface. The heat source is a nominal 100-W CO₂ laser operating on several discrete lines between a 10.51- and 10.63- μ m wavelength. The principal diagnostic is pressure, although a limited number of high-speed videos were made. The bottom of the chamber is closed with a Mylar-burst diaphragm. Experiments are typically terminated at about 17 MPa (2,500 psi).

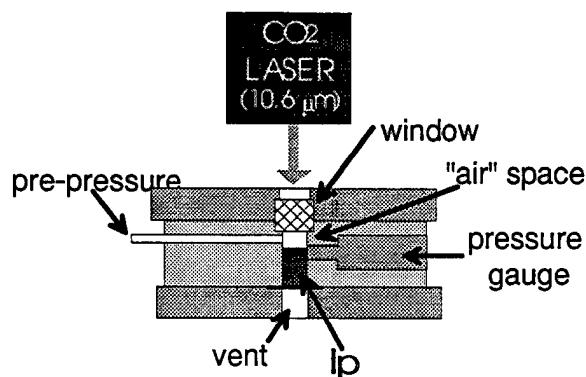


Figure 6. Schematic Drawing of Apparatus Used in Laser Heating of LP.

For these observations, the sample is prepressurized to the desired level and irradiated with the laser. Prepressures were measured with a mechanical gauge with 10-psi precision. After pre-pressurization, the chamber valve was closed. Possible decay in the pressure was judged to be negligible and always less than 50 psi, based on pressure-holding tests of the chamber using the piezoelectric gauge (Kistler model 211B, 5,000-psi full scale). The pressure behavior observed is reasonably reproducible; a typical record is shown in Figure 7 for two different heating rates at the same pressure level, near 7 MPa (1,000 psi). The laser heating starts at zero time and, in most cases, continues until the event is complete. As is seen in the figure, there is a characteristic delay where no pressure change is observed. At some point the reaction (gas generation) proceeds rapidly as measured by the pressure rise. The time to this rapid rise is the measured delay time. The pressure falls abruptly to atmospheric when the diaphragm bursts.

A series of preliminary observations of the time delay from the start of heating to the rapid pressure rise was made at two laser heating values by varying power and spot size at the sample. Typical results for 30 W in a 5-mm² spot (140 cal/cm²-s) and 30 W in 0.3-mm² area (2,400 cal/cm²-s) are shown in Figure 8. The observed values are plotted as a "rate" that is the inverse of the observed delay time. As can be seen from the figure, there is a much shorter delay or faster rate with both increasing flux and increasing pressure. The shortest delays in this set of data are about 2.5 ms. Although a linear fit is drawn through the points in Figure 8, no basis exists to expect any particular functional form.

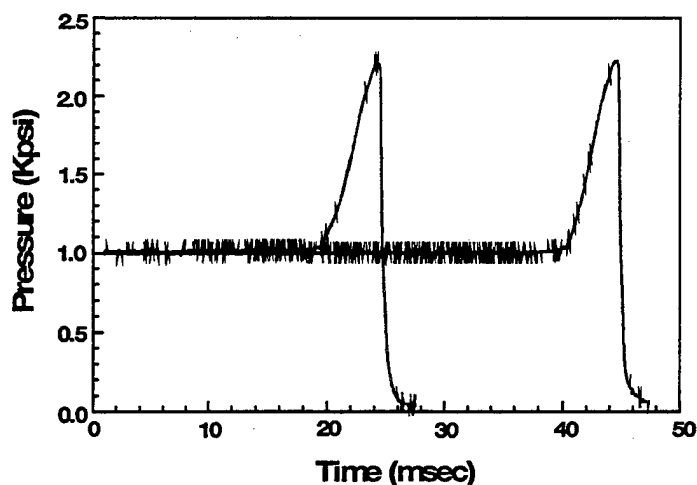


Figure 7. Typical Pressure-Time Records for Laser Heating at Two Different Heating Rates and Same Initial Pressure of 1,000 psi.

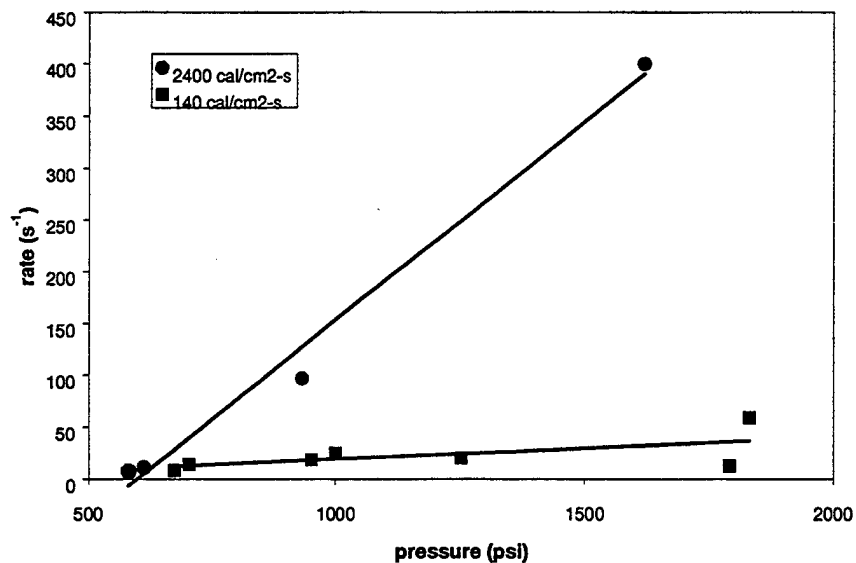


Figure 8. Plot of Rate of Reaction (Inverse of Delay Time) vs. Prepressurization at Two Heating Levels.

The extinction coefficient was measured for the XM46 at the laser wavelength by measuring the attenuation of thin layers of propellant tightly clamped between two ZnSe windows with precision spacers. Although scattering was expected to be negligible in this optically clear

liquid, the power meter was located close to the sample to minimize losses due to scattered light. The result was a value of 400 cm^{-1} , with an estimated total uncertainty of 20%. This value will depend upon the particular lines (wavelength) of a CO_2 laser and should therefore be used with care elsewhere. However, it was clear from even casual observation that the extinction was very high.

The laser beam power distribution at the liquid surface was measured with a Beamsan Model 3180 XFIR laser profiler (Photon, Inc., Santa Clara, CA). For these measurements, an optical path as similar as possible to that directing the light to the test chamber was used to direct the light to the profiler. A three-dimensional (3-D) plot and a contour plot with horizontal and vertical cuts is shown in Figure 9. As can be seen, the beam is not symmetric and has a noticeable tail. The power in the tail is less than 2% of the total beam power, and it was ignored in the analysis. With this assumption, Gaussian profiles were fit to several of the profiles. From these, it was determined that a value of $300 \pm 50 \text{ }\mu\text{m}$ for the standard deviation provided a reasonable fit to the beam measurements. (Note that, in the calculations, this value is specified as $600 \text{ }\mu\text{m}$ because of the definition of width in that program.) As seen, the scatter in the data is sufficient that error in the beam profile is not limiting the accuracy of the measured results.

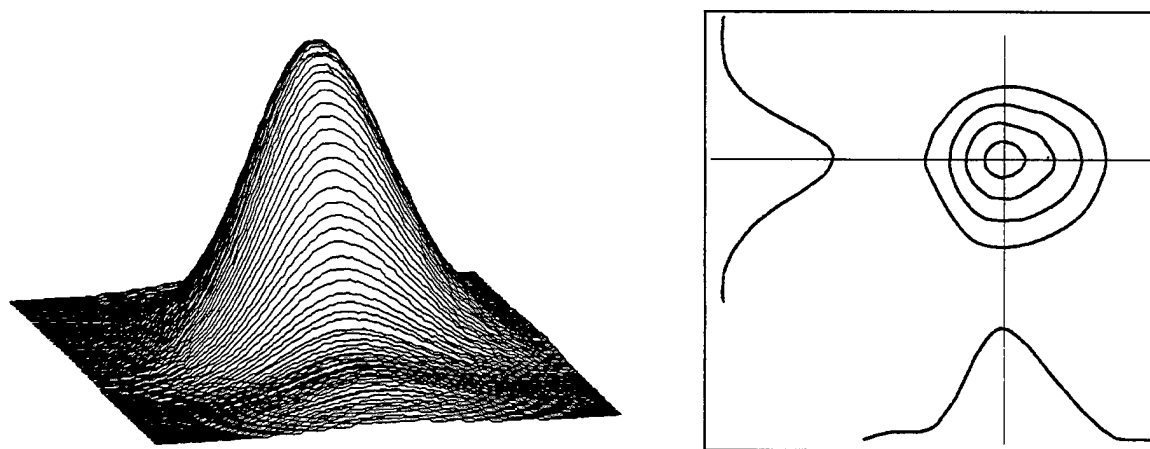


Figure 9. Profile of CO_2 Laser Beam Showing 3-D Plot (Left) and Contour With Two Cuts (Right).

The results of two series of observations at pressures of 6.9 MPa (1,000 psi) and 9.7 MPa (1,400 psi) yielded the reaction delays as listed in Table 1.

Table 1. Reaction Delays Observed at Two Pressures as Functions of Temperature

6.9 MPa		9.7 MPa	
Temperature (K)	Delay (ms)	Temperature (K)	Delay (ms)
2,320	4.97	2,915	7.00
1,848	2.64	2,833	14.5
1,302	4.42	2,786	14.5
1,290	7.22	2,525	6.9
835	7.70	1,992	14.9
—	—	1,664	29.4

3.3.2 Visualization of the Process. The strong pressure dependence implied by the values in Table 1 and Figure 8 were not expected. Although pressure effects are well-known in condensed phase reactions [7, 8] the pressures of the present observations are much less than usually applied to yield large change in rates. Thus, it was concluded as soon as the first variable pressure measurements were recorded that the process was possibly not behaving as expected. For this reason, the body of the apparatus was replaced with acrylic and a series of high-speed videos was made. Most of these were done at an initial pressure of 6 to 7 MPa (850 to 1,000 psi). A typical sequence taken at 500 frames/s is shown in Figure 10. The view in these images is from the side, similar to the “pressure gauge” in Figure 6. These images are made with strong back lighting; there is no emission from the event. This set was chosen as “average” with good clarity. Many reactions that were much faster were observed. The (naively) anticipated series of events was that the relatively small volume of XM46 near the surface would absorb the laser energy, rise to an ignition temperature, and generate a sufficient amount of gas to be recorded as a pressure rise. From the videos, it was observed that the surface does in fact react to become perhaps a two-phase zone, typically in times on the order of 1 ms. This reaction is shown as a disturbance to the meniscus in the first frame. Following a delay time with no further visible change, which is the dominant part of the observed delays, a rapid, approximately hemispherical reaction wave

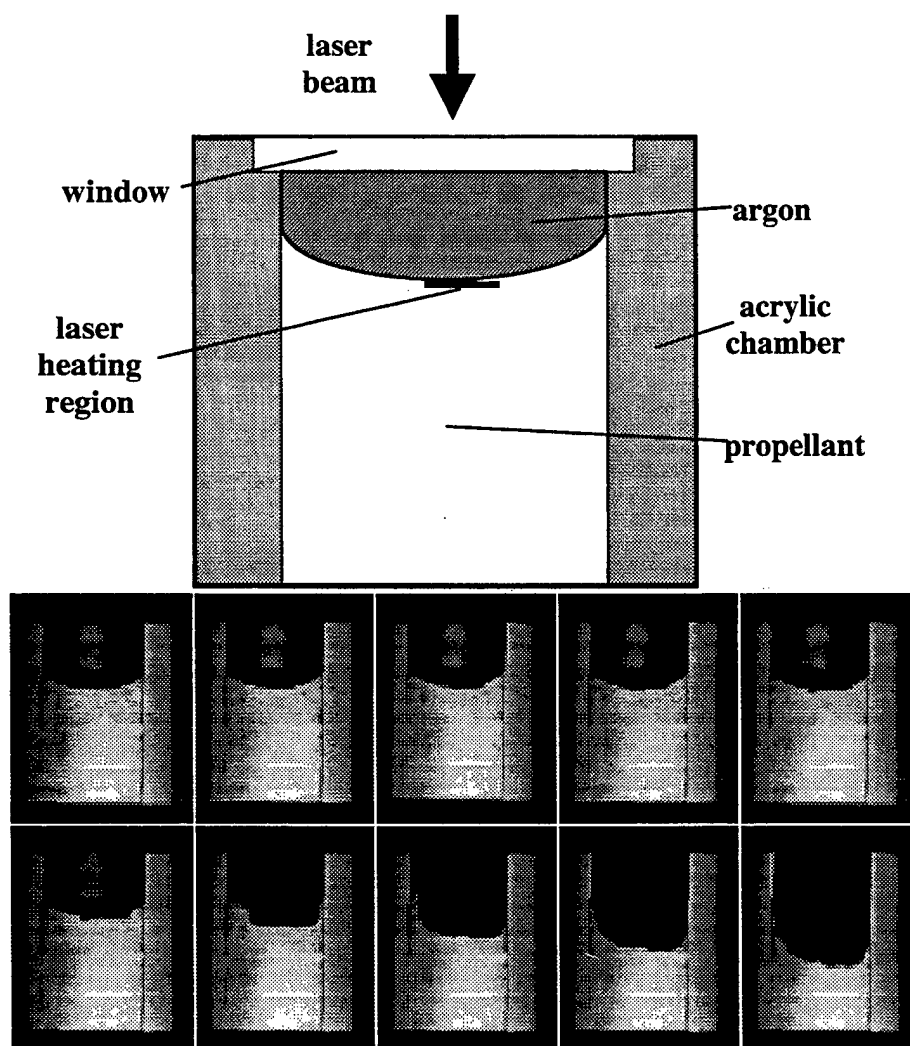


Figure 10. Schematic of Images and Frames From High-Speed Video of Laser-Heated XM46 at 1,000-psi Initial Pressure.

propagates through the remaining liquid. It is the gas generated from this event that was observed as the “ignition event” and recorded, as in Table 1. The amount of pressure rise from the first part of this sequence is too small to be recorded with the apparatus as configured. The delay times thus recorded and used in the kinetics analysis are for the induction time during which no major reaction is observed in the images.

The second interesting aspect of the rapid reaction wave is its apparent speed. The “burning rate” of HAN-based propellants, especially XM46, have been measured with some degree of

confidence [9, 10]. However, it has been known for some time that the surface must be stabilized to get reasonable rates at the pressures where ignition events are usually important. This has been done by the addition of a gel or, more recently [9, 10] by lowering the temperature. The numbers reported for the regression rate of the nonstabilized surface [11] have usually been met with some skepticism simply because they are so high that they must be dominated by hydrodynamic surface effects. As is seen here, the energy released in this reaction is also small, which is inconsistent with the very rapid rates. The rate of this wave has been measured from the videos. It is found to be a function of how the surface is "ignited," as well as of the initial pressure. In all cases, the rate of regression is seen to accelerate as the reaction proceeds. This effect may be due to the rapidly increasing pressure, or to other, possibly surface hydrodynamic, effects. A plot of the apparent velocity of the surface of the propellant vs. time is shown in Figure 11. During this record, the pressure increases from the initial value 7 MPa (1,000 psi) to near 15 MPa (2,200 psi). It is important to note that, in even the limited number of video records, there was a strong variation in this "rate," which depended not only on initial pressure but on the area of the surface irradiated. In general, higher pressure and igniting a larger fraction of the surface resulted in faster rates. The starting velocity values are comparable to those reported by Vosen [11], which were approximately 0.25 m/s at 7 MPa. However, from the present observations, it appears that geometry (surface area) may be important and a direct comparison may not be meaningful.

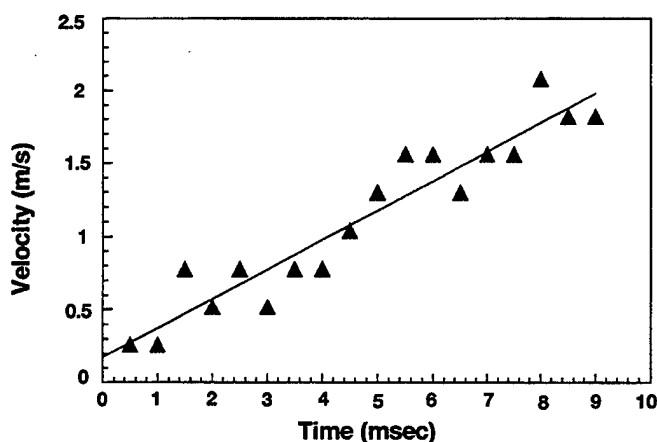


Figure 11. Surface Regression Velocity vs. Time for XM46 Taken From Video Record.

3.3.3 Analysis of Residual Liquid and Gas. In order to identify further the processes taking place in these experiments, the chamber was fitted with a vent tube that directed the vented gas and liquid into a 3-liter polyethylene sample bag. No attempt was made to purge the vent tube between the chamber and the (initially empty) sample bag, so a small amount of air is included in the samples. Even in experiments with similar heating-delay time characteristics, there were significant visual differences in the evolved liquid. The color of the liquid varied from clear (like virgin propellant) with many small bubbles to having a definite brown color. (Although they could be from gas generated during the reaction, the bubbles in the clear propellant are similar to those generated from the violent venting process without any heating.) As a preliminary approach to the analysis, one of each apparent extreme was analyzed. Because this project was not continued, these results are somewhat preliminary.

Gas samples were analyzed with a gas chromatography, mass spectroscopy, Fourier-transform infrared (GC-MS-FTIR) system (Hewlett Packard 5890 GC, 5970 MSD, 5965 IRD). A gas-tight syringe was used to transfer the gas from the sample bag to the gas chromatography (GC) injection port. The injector temperature was 200 °C; the GC was maintained at 50 °C for the duration of the run. The liquid residue was analyzed in single drops with Fourier-transform infrared (FTIR) microreflectance spectroscopy (Mattson Polaris FTIR interfaced to Spectra-Tech IR-Plan.). The recovered liquid was placed on aluminum foil and immediately analyzed. Comparison was made to unreacted propellant.

Analysis of the two gas samples showed masses 28 (N₂/CO), 32 (O₂), 40 (Ar), and 44 (CO₂/N₂O). The peak heights relative to mass 32 are shown in Table 2. The IR spectra of these samples showed only CO₂ and N₂O. No CO or NO was observed. While there is clearly more N₂O than CO₂ present in the IR spectra, the amount of CO₂ was far in excess of any that would have been present from air. This CO₂ indicates that there is some involvement of TEAN in the reactions. N₂O is a major expected product from HAN decomposition:

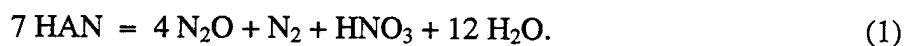


Table 2. Peak Heights From Mass Spectral Analysis of Gas Samples Following Laser Heating

Mass	Air	Sample No. 1	Sample No. 2
28	35	34	34
32	10	10	10
44	<0.05	3.0	2.8
30	0	1.3	1.2

The single-drop infrared (IR) spectra of the liquid were relatively poor in quality, but some differences in peak height were clear in comparison to unreacted XM46. The most noteworthy were the relative decrease in the intensity of the nitrate peak between 1,300 and 1,400 cm^{-1} , and the increase in the water peak near 1,600 cm^{-1} . While the peak near 1,600 cm^{-1} might also be attributed to the hydroxylammonium ion (HA^-), other peaks known to be due to HA^- were unchanged.

No new peaks were seen between 1,700 and 1,800 cm^{-1} , where oxidation products of the tri-ethanolammonium ion (TEA^+) would be most likely to appear.

4. Kinetics Analysis

4.1 Temperature Determination. Several diagnostic techniques were considered for measuring the temperature during these experiments. All were eliminated for reasons of complexity, lack of optical access, limited temporal or spatial resolution, or possible impact of the measurements due to material interactions with the propellant. Thus, the temperatures were calculated with a finite difference code using laser beam parameters and an optical absorption coefficient measured here and physical properties of the propellant from the literature. The loss in the laser power due to reflection from the surface was estimated to be 18% (82% transmitted into the liquid) of the measured power.

The beam was assumed to be Gaussian, with a sigma of 300 μm (full width of 600 μm). The extinction coefficient of the propellant at the laser wavelength was 400 cm^{-1} , as previously noted. A value [12] of 4.0 $\text{W/cm}^{\circ}\text{C}$ was used for the thermal conductivity. Although this value was measured over the range from 35–50 $^{\circ}\text{C}$, it was used over the entire calculation range.

The calculational grid was varied, and its effects were explored in detail, until making a smaller grid size no longer affected the temperature. The final grid used was finest at the laser absorption region with increasing cell size with radius and depth. Losses due to blackbody radiation from the surface were included in the calculations, although they were typically not important until the surface had been heated for several milliseconds. After the parameters had been explored sufficiently to have reasonable confidence that the calculation was describing the physical situation, a table was produced of surface-midpoint temperature vs. time for the incident power levels as recorded. The temperature numbers that are plotted in Figure 12 (as 1,000/temperature [1/T]) were taken from this table for the time corresponding to the observed event. The large values of the temperature numbers is probably a indication that the event was over driven; that is, the heat input was much greater than required with the kinetics limiting response.

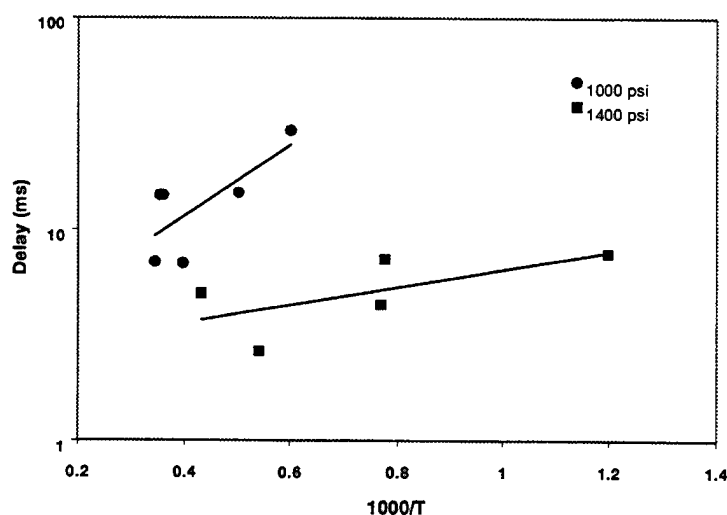


Figure 12. Plot of Delay vs. 1,000/T for the Calculation of Kinetic Parameters.

4.2 Kinetic Analysis. The reaction of the propellant was assumed to be first order and described by the Arrhenius equation

$$\text{rate} = \text{constant} \exp(-E_a/RT), \quad (2)$$

where E_a is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin. The observed parameter is the delay to reaction, which is proportional to the inverse of the rate. Thus, the equation can be rewritten as

$$\text{delay time} = C \exp(E_a/RT), \quad (3)$$

where C is a constant. A semi-log plot of delay time vs. $1/T$ will yield the constant C and the activation energy, E_a . For the data in Table 2, this plot is shown in Figure 12. A nonlinear, least squares fit was done to the exponential form to obtain the kinetics parameters. The results for the two pressures are given in Table 3. As can be seen in Figure 12, the data are quite noisy. In spite of these large uncertainties, there is clearly a major change in the behavior over this small pressure range.

Table 3. Kinetic Values From Data Fit

Pressure psi (psi) [MPa]	C	E_a (kcal/mol)	error (kcal/mol)
1,000 [6.9]	2.48	7.67	± 4.9
1,400 [9.7]	2.45	1.93	± 1.2

5. Discussion

5.1 Visualization. There are at least two interesting aspects to the "reaction wave" that propagates through the liquid after the delay time. The first observation is that the amount of liquid initially in the chamber and the pressure rise observed from the wave passing through most of the liquid are both known. If it is assumed that (1) the temperature does not increase

much, (2) most of the water in the LP remains liquid, and (3) the TEAN does not react (or reacts only slightly), it is deduced that there is only about one gas molecule generated for each molecule of HAN initially present. Thus, this reaction is consistent with the proposed first stage of LP reaction [1]. If this is the correct interpretation of the images, then the black clouds are primarily liquid drops of water-nitric acid solution (i.e., dilute nitric acid) and solid or liquid TEAN. The gas-phase nitrogen oxides should react rapidly with the TEAN [13], but this does not appear to happen on the time scale of these observations.

Vosen's conclusion that his measurements [11] were due to only the HAN reaction are verified by these observations. That is, even though the presence of a measurable amount of CO_2 is present in the gas phase products, the reaction is probably dominated by HAN decomposition. These observations are also in agreement with Klein's interpretation of his experiments [1].

The significance of this fast reaction in the ignition of XM46 in the RLPG is still not determined. Past studies of laser ignition of this propellant [9, 10] showed that, with rapid pressurization in a filled volume, it is possible to make a smooth transition to combustion.

5.2 Kinetics. Although the goals of this research effort had been to provide a good preliminary understanding of the "ignition kinetics" of XM46 by the present time, it is clear that the problem is not even well defined. The laser-heating studies show that, even at pressures near 13.5 MPa (2,000 psi), the propellant can react rapidly, with only a small part of the energy release and much of the products still in the liquid phase. This observation suggests that the self-pressurization in the enclosed DSC pans is responsible for the consumption of a large fraction of the sample in the rapid exotherm.

The temperature at which the LP reacts when heated "rapidly" may not be far above the "explosion temperature" of 230 °C. In the high-speed videos of the laser-heated experiments, the surface of the liquid thickens and suggests significant reaction in less than a millisecond. Thus, the calculated surface temperatures used in the kinetics analysis may be within the range of those observed in the slower explosion temperature observations at very early times. The careful

mapping of the time-temperature behavior of this first surface gasification might give a better measure of the liquid-phase reaction that starts the regression wave process. The apparent high temperatures calculated (and used for analysis) for heating before reaction might indicate that substantial heat is flowing into the remainder of the sample before the reaction begins. Determining whether this reaction no longer “hangs up” in the assumed liquid HAN reaction, where little heat is released, as the initial pressure is increased will also assist in understanding the processes in the gun.

Thus, the present understanding of the processes observed at pressures under 13 MPa (2,000 psi) could be described schematically, as shown in Figure 13. The kinetics of the first two steps are thought to be measured in this report; the delay measured is dominated by the second step. No observations of the third step with major energy release were made in this study; it is expected to be rapid at these pressures and above.

Although the heating rates are relatively low, it is still desirable to complete a reasonable DSC study of this material.

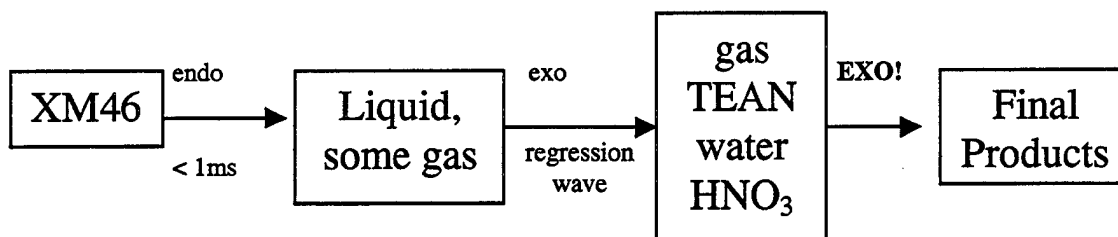


Figure 13. Schematic of Processes at Pressures Under 13 MPa (2,000 psi).

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6. References

1. Klein, N. "A Model for Reactions of the HAN-Based Liquid Propellants." ARL-TR-405, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, 1994.
2. Fifer, R. A., L. J. Decker, and P. J. Duff. "DSC Stability Test for Liquid Propellants." *22nd JANNAF Combustion Meeting*, CPIA 432, vol. II, pp. 203-211, 1985.
3. Wickstrom, L. Personal communication. Olin Corporation, Cheshire, CT, 1995.
4. Law, C. K. Final Report for Contract DAAG29-81-D-0100, DO 1596. July 1986.
5. Beyer, R. A., and G. P. Reeves. "Laser Ignition of Liquid Propellant XM46: Ignition of Larger Volumes." ARL-TR-1292, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, 1997.
6. Beyer, R. A. "Single Droplet Studies in a Hot, High Pressure Environment." BRL-TR-2900, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, 1988.
7. Weale, K. E. *Chemical Reactions at High Pressure*. London: Spon, 1967.
8. Neuman, R. C., Jr. "Pressure Effects as Mechanistic Probes of Organic Radical Reactions." *Accounts of Chemical Research*, vol. 5, pp. 381-387, 1972.
9. Vanderhoff, J. A. and, W. McBratney. "Burn Rate Investigations of Liquid Propellant XM46." *32nd JANNAF Combustion Symposium*, 1995.
10. McBratney, W. F., and J. A. Vanderhoff. "High Pressure Windowed Chamber Burn Rate Determination of Liquid Propellant XM46." ARL-TR-442, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, 1994.
11. Vosen, S. R. "The Burning Rate of Hydroxylammonium Nitrate-Based Liquid Propellant." *22nd Symposium (International) on Combustion*, pp. 1817-1825, 1988.
12. Dowler, W. L., N. W. Ferraro, M. S. Anderson, R. A. Beaudet, R. H. Frisbee, D. P. Maynard, C. M. Moran, and L. D. Strand. *Liquid Propellant XM46 Handbook*. Pasadena, CA: Jet Propulsion Laboratory, 1994.
13. Beyer, R. A. "Shock Tube Study of the Reaction of Triethanol Ammonium Nitrate With N_2O ." BRL-TR-3329, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, 1992.

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